GENERALIZED MASTER PLOTS AS A STRAIGHTFORWARD APPROACH FOR DETERMINING THE KINETIC MODEL: THE CASE OF CELLULOSE PYROLYSIS.

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Abstract

The thermal degradation of cellulose is a complex reaction and, despite the large amount of work by many investigators during the last decades, the actual understanding of the thermal decomposition kinetics is still very limited. Thus, while several mechanisms have been proposed to describe the process, the real model has not yet been clearly identified. In this paper, a set of experimental curves recorded under different heating schedules, i.e, linear heating rate, isothermal and constant rate thermal analysis (CRTA), has been analyzed using isoconversional and master plots methodology to discriminate the kinetic model followed by the reaction.

Keywords: Kinetics, Cellulose, Thermal degradation, Random Scission, Master Plots, Pyrolysis

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1. Introduction

A complete kinetic study of a solid state process requires the determination of the kinetic triplet; namely, the activation energy E, the preexponential factor A and the kinetic model *f(α)*. The determination of the latter constitutes, perhaps, the most delicate step, especially when dealing with highly complex reactions such as the degradation of polymers or natural compounds. The knowledge of the kinetic model driving a process provides a valuable insight regarding the reaction mechanism and it is useful for controlling a process, determining optimum processing temperatures or for aging studies. Procedures for determining the kinetic model most usually involve fitting the experimental data, obtained from a set of curves recorded under different heating profiles, into a predetermined set of kinetic models or equations [1]. Some of these models have been proposed considering certain theoretical assumptions regarding the geometry of the system or the reaction driving force while others are merely empirical fitting equations without any underlying physical meaning. However, the simultaneous fitting of experimental data proceeding from several curves to a single function is a moderately complex affair and requires the use of fitting programs. The use of master plots constitutes a simple and straightforward alternative for determining the kinetic model. Master plots are reference theoretical curves independent of the kinetic parameters, *E* and *A*, but dependent on the kinetic model [2, 3]. The method consists in transforming the experimental data into an experimental master plot, which is independent of the experimental conditions used for the experiment. Then, it is compared with the theoretical master plots, which are drawn by assuming certain kinetic models and serve as references. Thus, a simple graphical procedure is sufficient for determining the kinetic model followed by a reaction or, at least, the general type of

model. The main advantage of this approach is the lack of a previous assumption regarding the kinetic model followed by the reaction, thereby preventing errors arising from the fit to inappropriate kinetic models[4, 5]. The only requirements are the previous knowledge of the activation energy and that such parameter is maintained constant along the entire conversion range. Thus, the master plots method is usually employed together with isoconversional kinetic analysis procedures, which serve to evaluate whether the requirements are met [6-8].

The master plots approach might prove especially useful for studying the pyrolysis of natural materials, which degrade through complex reactions and for which finding the correct model has proven difficult. The degradation of cellulose is one of such cases, having attracted a great deal of attention in the last decades [9-17]. The decomposition of cellulose is a complex process involving complicated chemical pathways, mass and heat transfer phenomena and possible intermediates. Several models have been proposed for describing the reaction, including multistep kinetic models comprising several consecutive or competitive processes [18-20], simple first and n*th* order kinetic laws [12, 21-23], autoaccelerated models such as Avrami-Erofeev or Prout-Tompkins, commonly related to nucleation and growth mechanisms [10, 11, 22, 24, 25] and, recently, chain scission driven mechanisms [26]. The importance of determining the correct kinetic model is illustrated by the wide disparity in activation energies published in the literature [11, 15, 22, 26] which are most probably due to the nature of the sample, experimental errors and an incorrect selection of models.

Thus, in this work, the kinetics of cellulose pyrolysis has been studied by a combined isoconversional analysis and master plots procedure, showing that it is a fairly easy to

implement methodology, which does not require the use of complicated mathematical procedures and yet produce pretty accurate results despite the complexity of the process.

2. Experimental

Commercial microcrystalline cellulose from Aldrich, (product number 435236) was used for performing the study. Thermogravimetric measurements were carried out with a TA instruments Q5000 IR electrobalance (TA Instruments, Crawley, UK) connected to a gas flow system to work in inert atmosphere (150 mL min^{-1} N_2). Small mass samples (8-10 mg) were employed in order to minimize heat and mass transfer phenomena so that the kinetic parameters obtained are really representative of the forward reaction. Three different heating schedules were used to obtain the experimental data: linear heating rate at 1, 2, 5 and 10 K min^{-1}, isothermal runs at 533 and 548 K and CRTA at constant rates of 0.006 and 0.009 min^{-1}. Constant Rate Thermal Analysis (CRTA) consists in controlling the sample temperature in such a way that the reaction rate is maintained at a constant value, previously selected by the user, along the entire process. This way, by selecting a low enough decomposition rate, the mass and heat transfer phenomena occurring during the reaction are minimized. This advantage can prove especially valuable for studying the pyrolysis of cellulose, which seems to be quite susceptible to mass and heat inhomogeneities [9, 15]. As a consequence, the results obtained by CRTA are more representative of the forward reaction than those obtained from conventional methods such as linear heating programs or isotherms [27-29].

3. Theory

3.1 Theoretical background

The reaction rate, dα/dt, of a solid state reaction can be described by the following equation:

$$\frac{d\alpha}{dt} = A\exp(-E/RT)f(\alpha) \quad (1),$$

where A is the Arrhenius pre-exponential factor, R is the gas constant, E the activation energy, α the reacted fraction, T is the process temperature and $f(\alpha)$ accounts for the reaction rate dependence on α. The kinetic model $f(\alpha)$ is an algebraic expression which is usually associated with a physical model that describes the kinetics of the solid state reaction. Table 1 lists the functions corresponding to the most commonly used mechanisms found in literature. In this work, the reacted fraction, α, has been expressed with respect to the degradable part of the cellulose, as defined below:

$$\alpha = \frac{w_0 - w}{w_0 - w_f} \quad (2),$$

where w_o is the initial mass of cellulose, w_f the mass of residual char and w the sample mass at an instant t .

Eq. (1) is a general expression that describes the relationship among the reaction rate, reacted fraction and temperature independently of the thermal pathway used for recording the experimental data. Thus, experimental data extracted from all runs, whatever the heating profile, can be simultaneously fitted by Eq. (1).

126 *3.2. Isoconversional Analysis*

127 Isoconversional methods, also known as "model-free", are used for determining the
128 activation energy as a function of the reacted fraction without any previous assumption
129 on the kinetic model fitted by the reaction. The Friedman isoconversional method is a
130 widely used differential method that, unlike conventional integral isoconversional
131 methods, provides accurate values of the activation energies even if they were a
132 function of the reacted fraction [6]. Eq. (1) can be written in logarithmic form:

133 $$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(Af(\alpha)\right) - \frac{E}{RT} \quad (3)$$

134 At a constant value of α, $f(\alpha)$ would also be constant and Eq. (3) could be written in the
135 form:

136 $$\ln\left(\frac{d\alpha}{dt}\right) = Const - \frac{E}{RT} \quad (4)$$

137 The activation energy at a constant α value can be determined from the slope of the plot
138 of the left hand side of Eq. (3) against the inverse of the temperature, at constant values
139 of α.

140

141 *3.3. Determination of the kinetic model by means of generalized master plots*

142 It has been shown that universal master plots, valid for experimental data recorded
143 under any heating profile, can be obtained by the introduction of the generalized time, θ,
144 defined as [2, 3, 30]:

$$\theta = \int_0^t \exp\left(\frac{-E}{RT}\right) dt \quad (5),$$

that can also be written:

$$\frac{d\theta}{dt} = e^{\frac{-E}{RT}} \quad (6),$$

that after substitution into Eq. (1) leads to:

$$\frac{d\alpha}{d\theta} = Af(\alpha) \quad (7)$$

From Eq. (7) and taking α = 0.5 as a reference it follows:

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{0.5}} = \frac{f(\alpha)}{f(0.5)} \quad (8)$$

Eq. (8) shows that for a given α, the reduced-generalized reaction rate, $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$, is equivalent to $f(\alpha)/f(0.5)$ if the proper $f(\alpha)$ is considered.

Additionally, the generalized reaction rate can be written as:

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt}\exp\left(\frac{E}{RT}\right) \quad (9)$$

Thus, the relationship between the generalized reaction rate and the experimental data can be established:

159 $$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{0.5}} = \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} \frac{\exp(E/RT)}{\exp(E/RT_{0.5})} \quad (10),$$

160 being $T_{0.5}$ the temperature corresponding to α= 0.5. The equation above implies that, for
161 experimental data recorded under non isothermal conditions, the knowledge of the
162 activation energy is required to construct the experimental master plots. Alternatively,
163 in the case of isothermal conditions, the previous knowledge of the activation energy is
164 no longer required and Eq. (10) is simplified to:

165 $$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{0.5}} = \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} \quad (11)$$

166 It is possible to deduce the kinetic model the reaction obeys by simply comparing the
167 plot of the generalized reaction rate vs. the reacted fraction, as calculated from the
168 experimental data and Eq. (10), with the plots corresponding to the different theoretical
169 solid state reaction models, as deducted from the fraction *f(α)/f(0.5)* (Eq. (8)). The plots
170 mastering the kinetic models represented in Table 1 are shown in Fig. 1, including the
171 very recently proposed random scission models [3, 31].

172 *3.4. The random scission kinetic model*

173 This model for depolymerisation processes was initially developed by Simha-Wall for
174 the case of polyethylene. The model implies the random cleavage of the bonds,
175 following first order kinetics, along the polymer chains, producing fragments of
176 progressively shorter lengths that are eventually released when their size is small
177 enough to evaporate [32]. However, given that most degradation reactions are studied
178 by thermogravimetry, a relationship between the fraction of bonds broken and the mass
179 lost by volatilization must be established before the model can actually be applied.

Thus, in a recent work, the model was reformulated to facilitate their use with conventional kinetic methods [31] and the following conversion function was proposed:

$$f(\alpha) = L(L-1)x(1-x)^{L-1} \quad (12),$$

where x and L are the fraction of bonds broken and the minimum length of the polymer that is not volatile, respectively. Unfortunately, Eq (12) only has a symbolic solution for L=2. The problem can be sorted out by calculating numerically the f(α) functions for L≠2, just by giving values to both L and x.

4. Results and Discussion

Fig. 2 shows a set of α-T curves corresponding to the thermal degradation of microcrystalline cellulose. Experiments were carried out using three different heating schedules: linear rise in temperature (Fig. 2a), isothermal (Fig. 2b) and constant reaction rate (Fig. 2c). The curves have been constructed from the thermogravimetric experiments using Eq (2) to determine the α values. It should be noted that after the main degradation step, involving the loss of more that 90% of the initial mass, the mass keeps decreasing but at a much reduced rate so it is difficult to set a clear value for w_f. Such behaviour is clearly illustrated in Figure 2a where a stable plateau at α=1 is not reached. Thus, a final residue of 8,5% of the initial mass was assumed as w_f. The curves recorded under linear rise in temperature show the typical sigmoidal shape of any kinetic curve obtained under this kind of temperature schedule. Isothermal runs were

performed by quickly heating up to the target temperature, in such a way that the mass loss during the heating up was negligible. The isothermal curves also present a sigmoidal shape, with the inflection point located during the early stages of the degradation, which is indicative of an "acceleratory" type model such as nucleation or chain scission. That is confirmed by the differential curves, which display a maximum at low reaction times. Additionally, the CRTA curve in Fig. 2c shows a temperature minimum in the T-α plot. As it has been previously shown, there is a direct relationship between the shape of the CRTA curves and the kinetic mechanism followed by a reaction [33, 34]. Thus, such temperature minimum indicates that an autoacceleratory process drives the reaction [33], in concordance with the observations made from the isothermal experiments. Although curves in Figure 2 seem to suggest a simple step process and master plots method could be used to determine the kinetic model, the value of the activation energy for the process must be established first. To that end, the Friedman isoconversional method, detailed in Section 3.2, is selected because it combines simplicity and precision [6]. Fig. 3 shows the Friedman plots constructed by plotting the left hand side of Eq. (3), $ln(d\alpha/dt)$, against the inverse of the temperature at several constant α values using experimental data extracted from all curves in Fig. 2 simultaneously. From the slope of the Friedman plots the activation energy as a function of the conversion can be calculated, as shown in Fig. 4. It is clear that the activation energy remains fairly constant along the conversion range, indicating a simple process that can then be described by a single f(α) function. The activation energy lies in the range of 190-192 kJ mol^{-1}, so an average value of 191 kJ mol^{-1} can be established. However, a significant deviation appears at conversion values over 0.9, accompanied with large standard errors and poor correlation factors. This can be attributed to several causes. For example, it has been claimed before that cellulose pyrolysis consists of two

227 consecutive steps, the first one being responsible of the majority of the degradation. [11,
228 26]. Alternatively, it has also been proposed that the residual char left after the main
229 pyrolysis step keeps degrading at a very slow rate due to traces of oxygen present on the
230 system [11, 13, 26]. In any case, the variance in the activation energy affects only a very
231 limited fraction of the total conversion range and does not invalidate the use of the
232 master plots methodology for determining the kinetic model followed by the reaction.

233 The generalized master plots are independent of the heating profile under which the
234 experimental data are recorded. They depend exclusively on the kinetic model obeyed
235 by the reaction. Thus, in principle, the experimental master plots obtained under
236 different heating profiles should take similar shapes. The master plots are constructed
237 individually for every experimental curve by plotting the right hand side of Eq. (10) vs.
238 the conversion, α, using the activation energy previously obtained from the
239 isoconversional analysis, 191 kJ mol^{-1}, and the experimental values of $d\alpha/dt$ and T
240 corresponding to each curve. Likewise, the theoretical master plots corresponding to the
241 different kinetic models included in Table 1 are built by plotting the right hand of Eq.
242 (8) against the conversion α. Fig. 5 shows the comparison between the theoretical and
243 experimental master plots constructed using the experimental data from every curve in
244 Fig. 2. All master plots, regardless of the heating profile under which the experimental
245 data is recorded, match closely the theoretical plot corresponding to a random scission
246 kinetic model. Such conclusion is consistent with the isothermal experiments in Figure
247 2b, which display a maximum in the differential curves at low reaction times, typical
248 from random scission models [31]. Likewise, the CRTA experiments in Figure 2c show
249 a minimum in the T-α plot at α values around 0.25, also characteristic of such models
250 [33]. The model is also supported by a previous study carried out using a more complex

kinetic procedure [26]. The kinetic models defining random chain scission mechanisms were recently introduced and since that time, they have been found to describe several polymer degradation reactions [3, 31, 33]. The model assumes that the cleavage of bonds occurs randomly along the polymeric chains, followed by the volatilization of the fragments once they are small enough. This model seems especially suitable to cellulose degradation, which has been described to proceed by depolymerisation by transglycosylation [10, 21, 26, 35].

It should be emphasized that the chain scission model has been concluded without any previous assumption regarding the reaction kinetic mechanism and using a methodology that does not require the use of complicated fitting programs. This constitutes an interesting advantage since model-fitting procedures entails fitting the experimental data to a predetermined set of models which may or may not include the real one. Moreover, such models (the most commonly used are included in Table 1) were developed assuming very restricted conditions regarding the homogeneity and geometry of the system and the force driving the reaction. In real systems, deviations from such ideal conditions are expected and they may alter the conversion function [36], thereby difficulting the use of model-fitting methods and increasing the chances an inappropriate model is selected. On the other hand, the generalized master plots constructed from experimental data are faithful to the real system and would allow discerning whether the reaction under study follows a theoretical model or deviates from such ideal situations.

5. Conclusions.

This paper explores the kinetics of cellulose thermal degradation under a combined isoconversional and generalized master plots approach. The activation energy for the

pyrolysis was estimated at 191 kJ mol^{-1} and it was found that a chain scission kinetic model governs the reaction. Such model provides a suitable physical description of the degradation mechanism of cellulose. The analysis methodology here employed is very simple to implement, not requiring the use of complex fitting programs or computational power, yet provides accurate results, which are consistent with recent findings in cellulose degradation. Additionally, this methodology implies no assumption whatsoever regarding the kinetic model obeyed by the reaction thereby avoiding the risks of fitting the experimental data to an improper kinetic model.

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Figure Captions

Fig. 1 : Generalized master plots corresponding to the different kinetic models in Table 1 as constructed from Eq. (8): (a) Random scission models; (b) diffusion controlled models; (c) "n order" models and (d) nucleation and growth models.

Fig. 2: Experimental curves (dotted lines) obtained for the thermal decomposition of microcrystalline cellulose under N_2 gas flow and the following experimental conditions: (a) linear heating rate of 1, 2, 5 and 10 K min^{-1}; (b) isotherm at 533 and 548 K; and (c) CRTA degradation rate of 0.006 and 0.009 min^{-1}.

Fig. 3: Friedman plots resulting from the simultaneous model-free analysis of all the experimental curves included in Fig 2 corresponding to cellulose pyrolysis under different experimental conditions; linear heating rate, isothermal and controlled reaction rate.

Fig. 4: Evolution of the activation energy with the conversion obtained using the Friedman isoconversional method according to Eq. (4).

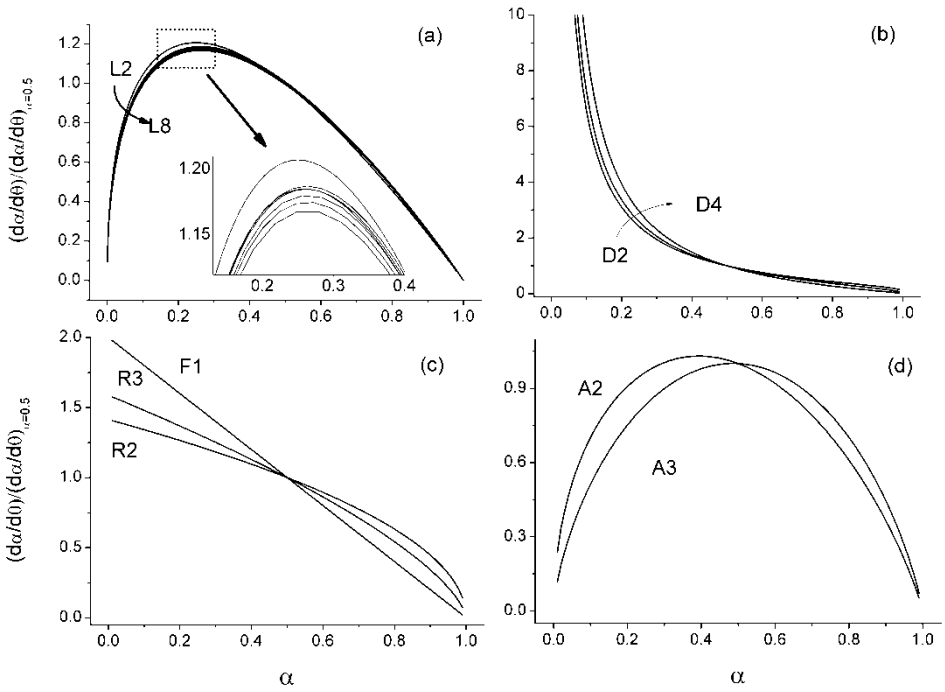
Fig. 5: Comparison between theoretical master plots constructed from the ideal kinetic models in Table 1 and the generalized master plots built from experimental curves recorded under (a) linear heating rate, (b) isothermal conditions and (c) controlled reaction rate.

409 **TABLE 1.** *f(α)* kinetic functions for the most widely used kinetic models, including the
410 newly proposed random scission model.

Mechanism	Symbol	f(α)
Phase boundary controlled reaction (contracting area)	R2	$2(1-\alpha)^{1/2}$
Phase boundary controlled reaction (contracting volume)	R3	$3(1-\alpha)^{2/3}$
First order law or random nucleation followed by an instantaneous growth of nuclei. (Avrami-Erofeev eqn. n =1)	F1	$(1-\alpha)$
Random nucleation and growth of nuclei through different nucleation and nucleus growth models. (Avrami-Erofeev eqn ≠1.)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$
Three-dimensional diffusion (Jander equation)	D3	$\frac{3(1-\alpha)^{2/3}}{2\left[1-(1-\alpha)^{1/3}\right]}$
Three-dimensional diffusion (Ginstling-Brounshtein equation)	D4	$\frac{3}{2\left[(1-\alpha)^{-1/3}-1\right]}$
Random Scission L=2 [31]	L2	$2\left(\alpha^{1/2}-\alpha\right)$
Random Scission L>2 [31]	Ln	No symbolic solution

411 **FIGURE 1**

412



413

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416 models; (c) "n order" models and (d) nucleation and growth models.

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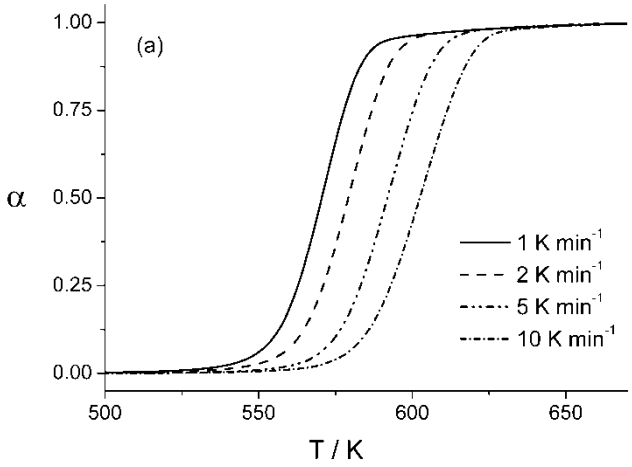
424 **FIGURE 2**



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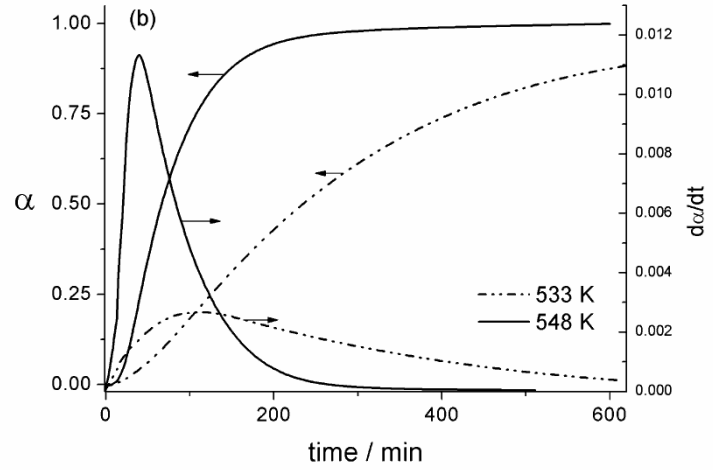

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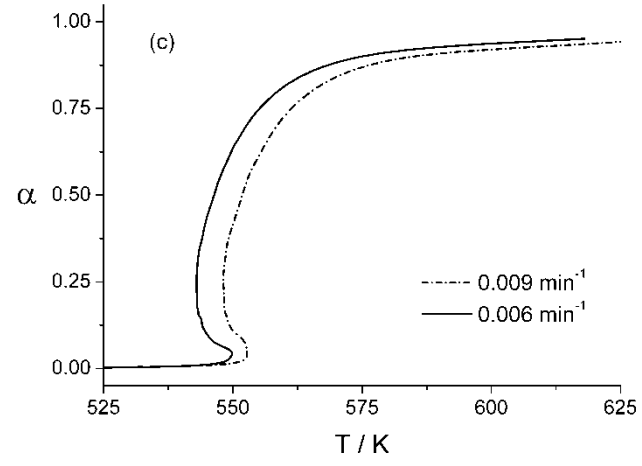

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Fig. 2: Experimental curves (dotted lines) obtained for the thermal decomposition of microcrystalline cellulose under N_2 gas flow and the following experimental conditions: (a) linear heating rate of 1, 2, 5 and 10 K min^{-1}; (b) isotherm at 533 and 548 K; and (c) CRTA degradation rate of 0.006 and 0.009 min^{-1}.

FIGURE 3

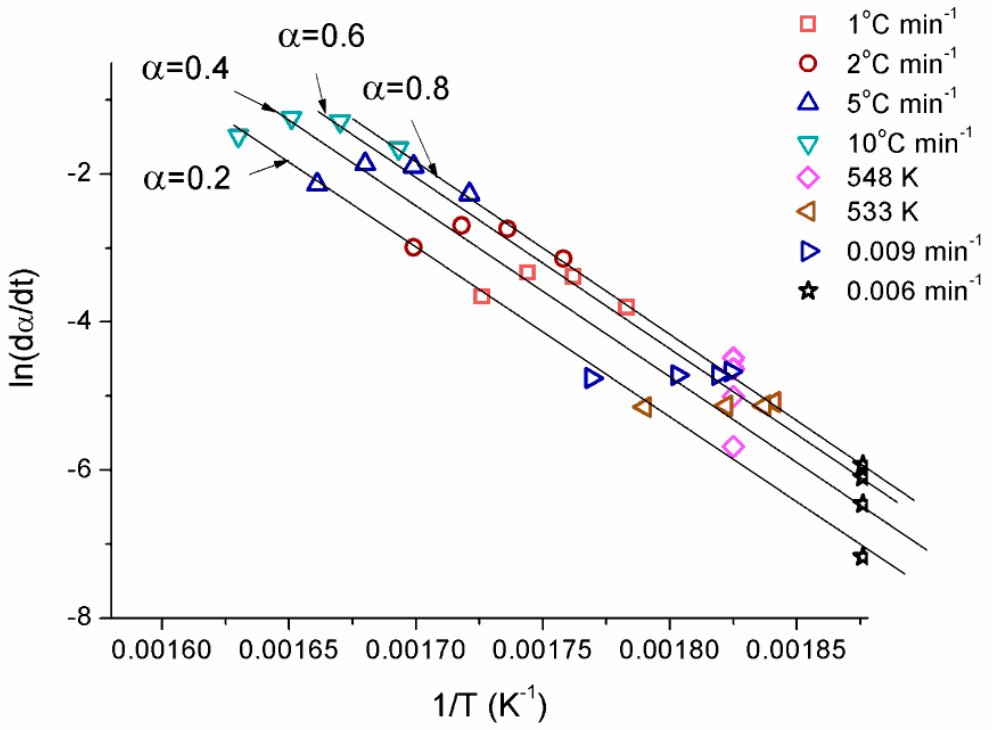

Fig. 3: Friedman plots resulting from the simultaneous model-free analysis of all the experimental curves included in Fig. 2 corresponding to cellulose pyrolysis under different experimental conditions; linear heating rate, isothermal and controlled reaction rate.

441 **FIGURE 4**

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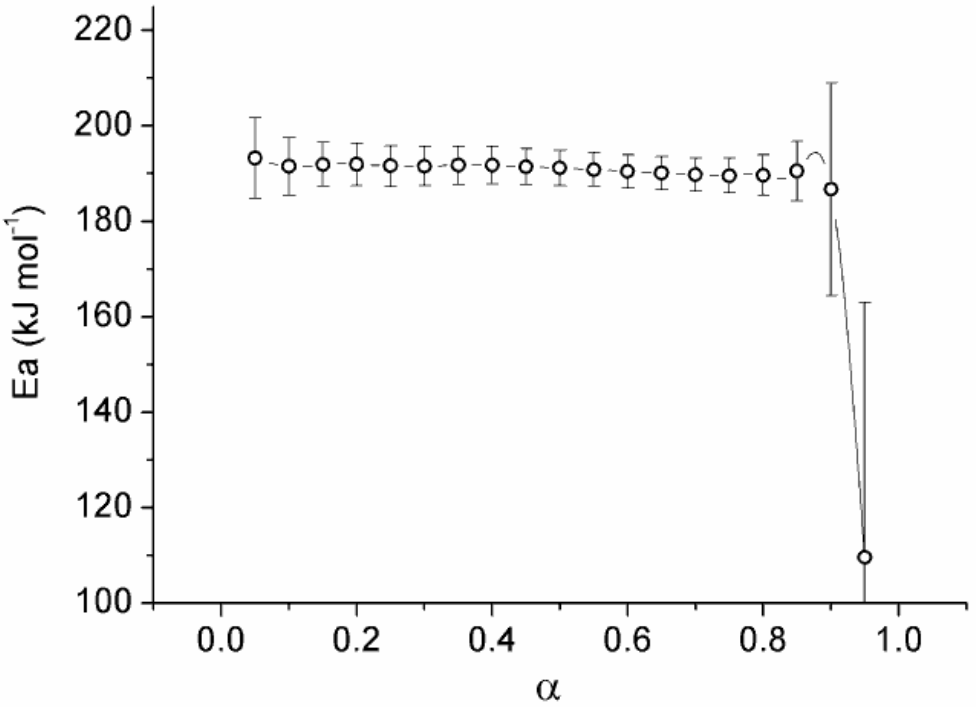

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445

446 **Fig. 4:** Evolution of the activation energy with the conversion obtained using the

447 Friedman isoconversional method according to Eq. (4).

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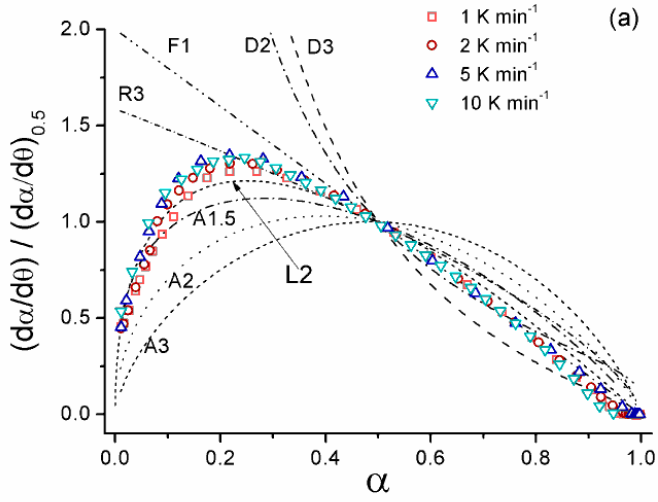
453 **FIGURE 5**



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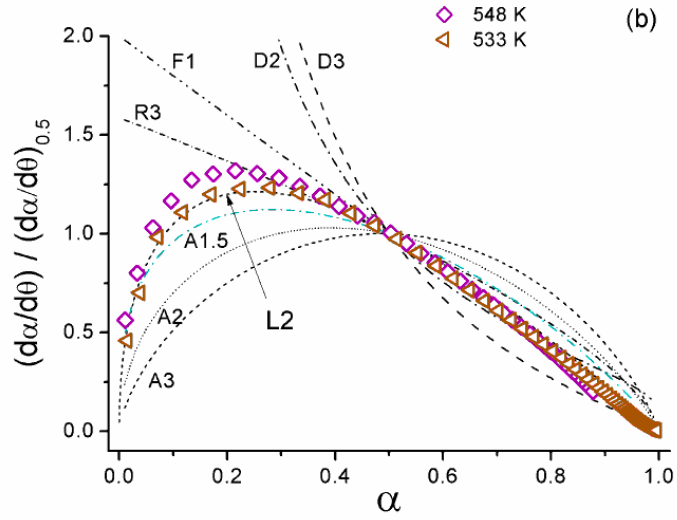

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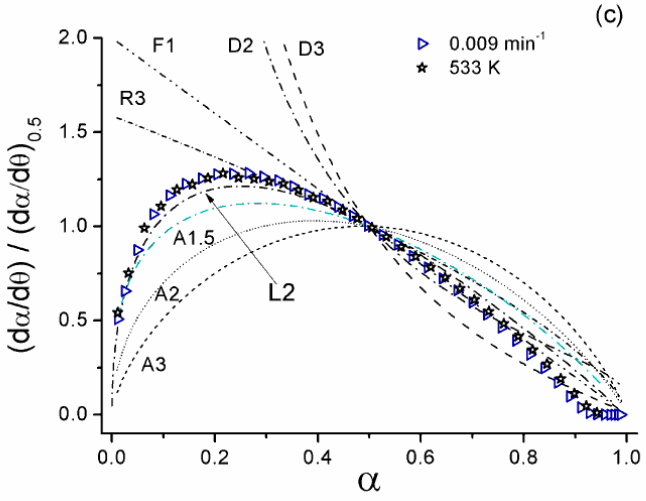

456

457 **Fig. 5:** Comparison between theoretical master plots constructed from the ideal kinetic
458 models in Table 1 and the generalized master plots built from experimental curves
459 recorded under (a) linear heating rate, (b) isothermal conditions and (c) controlled reaction
460 rate.

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